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# Adsorption of Phosphorus Using Cockle Shell Waste

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**ABSTRACT:** Phosphorus is an essential nutrient for aquatic plants and animals. The acceptable range for phosphorus in water is from 0.01 to 0.03 mg/L. However, excessive phosphorus use can result in biodiversity loss and pollution and endanger aquatic creatures and human health because the pollutants are non-biodegradable and thus accumulate over time. This work investigated the removal of phosphorus from synthetic wastewater containing $KH_2PO_4$ via adsorption using calcined cockle shell waste. Phosphorus adsorption by calcined cockle shell waste of less than 75 µm particle size was investigated. Five different adsorbent dosages (0.2, 0.4, 0.6, 0.8, and 1.0 g) mixed with 10 ppm phosphate were adsorbed for 60 min. The presence of calcined cockle shell waste was determined by using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and a DR6000 UV–visible spectrophotometer. In brief, the highest dosage of 1.0 g removed 94.96% phosphorus from the synthetic wastewater, while the longest treatment time resulted in 95.74% phosphorus adsorption. The proposed method is low-cost and convenient.

**KEYWORDS:** Cockle shell; phosphorus; eutrophication; adsorption; interval time

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## 1. Introduction

Agriculture has increased the amount of phosphorus discharged into surface water. Crop fertilisation releases phosphorus into the nearby aquatic ecology, where it is a vital nutrient that promotes the growth of biological organisms and algae [1]. The permissible limit of phosphate in water is between 0.01 and 0.03 mg/L [1,2]. However, the nonstop demand economy of agriculture has caused excess phosphorus discharge, leading to environmental degradation, including water pollution. The uncontrolled amount of phosphorus discharged accelerates eutrophication and algal blooms. This situation causes an increase in the biochemical oxygen demand (BOD) and the failure of aquatic ecosystems, which endanger human health and other organisms.

Cockleshells (*Anadara granosa*), which live behaviourally buried in the sediment, have grown in importance as a valuable ecological marine product in Malaysia, particularly on the west coast of West Malaysia. Cockles contribute to about 93% of marine aquaculture production [3,4]. The local cockle shells, '*kerang*', are classified under the phylum Mollusca, class Bivalvia, order Arcoida, and family Arcidae [5]. Cockles are an affordable source of protein and are broadly distributed in Southeast Asian countries [6]. They produce an abundance of shell waste that is dumped into landfills or along the seashores due to the expensive disposal procedure. The high amount of untreated cockle shell waste leaves an unpleasant odour and visual disturbance to the surroundings. Excessive amounts of phosphorus can be treated with the adsorption method [1]. This process is advantageous as it is easy to handle. Calcined cockle shell waste contains more than 95% calcium carbonate ($CaCO_3$) by weight. They can be used as a low-cost adsorbent material as they have shown good performance for the removal of organic and inorganic matters in polluted water [6]. Through calcination or thermal decomposition, $CaCO_3$ is converted to calcium oxide, CaO. CaO is an alkaline earth oxide and it can be used for industrial wastewater and sewage treatment.

The primary goal of this research is to assess the performance of the powdered form of calcined cockle shell for phosphorus removal. Phosphorus-rich synthetic wastewater was treated with the calcined sample under an appropriate temperature to investigate the effects of different dosages and treatment times. Cockleshell waste has the potential to be used as an adsorbent for removing phosphate ($PO_4^{3-}$) in polluted water, thereby reducing a source of eutrophication. In addition, the removal of phosphorus from water bodies benefits the environment.

## 2. Materials and Methods

### *2.1. Adsorbent*

Cockle shells (*Anadara granosa*) were collected from Teluk Kerang, Pontian. The cockle shells were cleaned using tap water and brushes to remove any debris. Then, the shells were boiled for 10 min at 100 °C before being air-dried at room temperature. The cockle shells were then dried in a drying oven at 110 °C for 2 h to ensure complete drying before being crushed with a pestle and mortar. The shell was ball-milled using the dry-milling method for 45 min at 500 rpm. Subsequently, the resultant microsized powder was sieved using a stainless steel laboratory filter with an aperture of 75 µm. Finally, the powder was calcined in a chamber furnace and stored in a ziplock bag [7,8]. Figure 1 shows the overall process of adsorbent preparation.

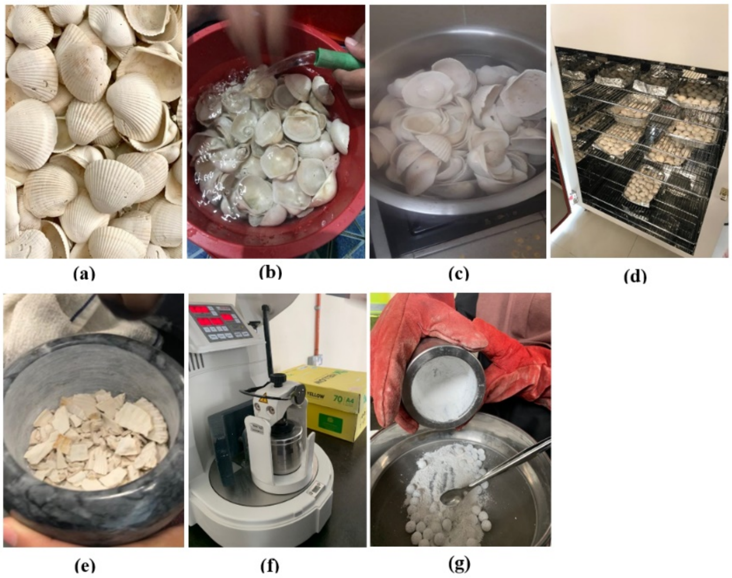
(a) (b) (c) (d)
(e) (f) (g)

**Figure 1.** The process of preparation of adsorbent: (a) Collecting, (b) cleaning, (c) boiling, (d) drying, (e) crushing, (f) grinding, and (g) sieving.

### *2.2. Adsorbate*

To produce the synthetic solution to test the adsorption process, 0.1433 g of anhydrous potassium phosphate ($KH_2PO_4$) was dissolved in 1 L of deionised water (DI) to make a 100 ppm stock solution in a volumetric flask. Then, 500 mL of the stock solution was diluted with 500 mL of DI in another volumetric flask, bringing the concentration to 50 ppm. Finally, in a volumetric flask labelled as 10 ppm, 200 mL of a 50 ppm solution was diluted with 800 mL of DI to make a phosphate solution at the desired experimental concentration of 10 ppm.

### *2.3. Chemicals*

Molybdate and amino acid were used to measure the concentration of the various phosphate solutions. The concentration of the phosphate solutions was determined using a DR6000 UV–visible spectrophotometer and the reagents.

### *2.4. Characterisation*

The calcined cockle shells (CCS) were subjected to various analyses. The image of the cockle pores before and after calcination was captured using SEM (EM-30AX Plus). The functional group was determined using Fourier-transform infrared spectroscopy (FTIR; PerkinElmer Spectrum Two™ IR spectrometer). A DR6000 UV–vis spectrophotometer (Hach DR6000 Benchtop Spectrophotometer) was used to figure out the initial and final concentrations of the adsorbate).

### *2.5. Adsorption studies*

The best method for removing phosphorus from synthetic wastewater is via the adsorption process. After the process of adsorption in a orbital shaker, the adsorbate and adsorbent were separated using filter paper. The adsorbate of 25 mL of potassium phosphate was added with 1 mL of molybdate reagent and 1 mL of amino acid reagent. The final concentration of phosphorus solution was measured using the UV-vis spectrophotometer (Figure 2). The percentage of removal efficiency, as well as the phosphorus sorption capacity, were calculated.

(a) (b) (c)

**Figure 2.** (a) Incubator shaker, (b) the reagents used for determining phosphorus concentration, (c) DR6000 UV–vis spectrophotometer.

#### *2.5.1. Effect of Different Amounts of Dosage of Adsorbent*

Various adsorbent dosages were tested to determine the best dosage for phosphate adsorption in synthetic wastewater. Different dosages of CCS adsorbent (0.2, 0.4, 0.6, 0.8, and 1.0 g) was added to a set of conical flasks containing 100 mL of 10 ppm phosphate solution. The solution–adsorbent mixtures were then incubated for 60 min in an incubator shaker set to 37 °C and 150 rpm [9]. The phosphate removal effectiveness (E) and sorption capacity (q) of various adsorbent dosages were calculated using Eqs. 1 and 2.

$$E\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{Eq. 1}$$

where E stands for removal efficiency. $C_i$ denotes the initial phosphate concentration (mg/L) and $C_f$ denotes the phosphate concentration after adsorption (mg/L).

$$q = \frac{V\ (C_i - C_f)}{m} \qquad \text{Eq. 2}$$

where q is adsorption capacity (mg/g). $C_i$ is the initial phosphate concentration (mg/L). $C_f$ is the final phosphate concentration in the solution (mg/L), m is adsorbent mass (g), and V the volume of the solution (L).

### *2.5.2. Effect of Treatment Time*

The treatment time was varied to determine the best time for phosphorus adsorption in the synthetic wastewater solution. Various durations of 20, 30, 40, 50, and 60 min were used for the test. The other experimental conditions were kept constant with a 10 ppm initial concentration of phosphate solution and 1.0 g of CCS for adsorbent dosage. The samples were placed on an incubator shaker with a 150 rpm agitation at a constant temperature of 37 °C.

## 3. Results and Discussion

### *3.1. The Calcination Process of Cockle Shell*

The cockle shells were weighed using an analytical balance before the calcination process. Usually, the temperature range for calcination is 700–900 °C to obtain the perfect porosity. The porosity makes the adsorption more efficient since it increases the surface area of the adsorbent. The cockle shells were calcined in a chamber furnace (Carbolite Gero 30–3000 °C) at 900 °C for 2 h [10]. The calcination process used a heating rate of 27 °C/min. Before being placed in the furnace chamber, the powder was poured into the crucible. The weight of the calcined cockle shell (CCS) powder decreased. The purpose of the calcination process was to convert $CaCO_3$ from the crab shell to CaO. Eq. 3 shows the reaction undergone by $CaCO_3$ during the calcination process, in which it is converted to CaO. The porosity makes the adsorbents have more surface area, which makes the percentage of adsorption go up.

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{Eq. 3}$$

This equation shows how $CaCO_3$ changes after being heated and calcium carbonate transforms into calcium oxide.

### *3.2. Fourier-Transform Infrared Spectroscopy (FTIR)*

FTIR was conducted to determine the presence of functional groups of $CaCO_3$ in the raw cockle shell sample and CaO in the calcined cockle shell sample. Figure 3 shows the bands in the IR spectra with an absorption range of 400–4000 $cm^{-1}$. Different types of bonds are commonly absorbed in their range of region since the function of the FTIR is to identify the functional group. For calcined cockle shells, the characteristic FTIR bands were observed at 710.89, 871.22, 1395.00, and 3641.07 $cm^{-1}$. For the treatment time experiment, the prominent bands were at 711.70, 871.42, and 1393.40 $cm^{-1}$. Meanwhile, for the dosage experiment, 1.0 g was chosen as the suitable dosage. The characteristic bands were observed at 711.61, 871.34, and 1393.36 $cm^{-1}$. The difference between the three spectra was the observation of a new peak on the calcined cockle shell absorption spectrum at 3641.07 $cm^{-1}$.

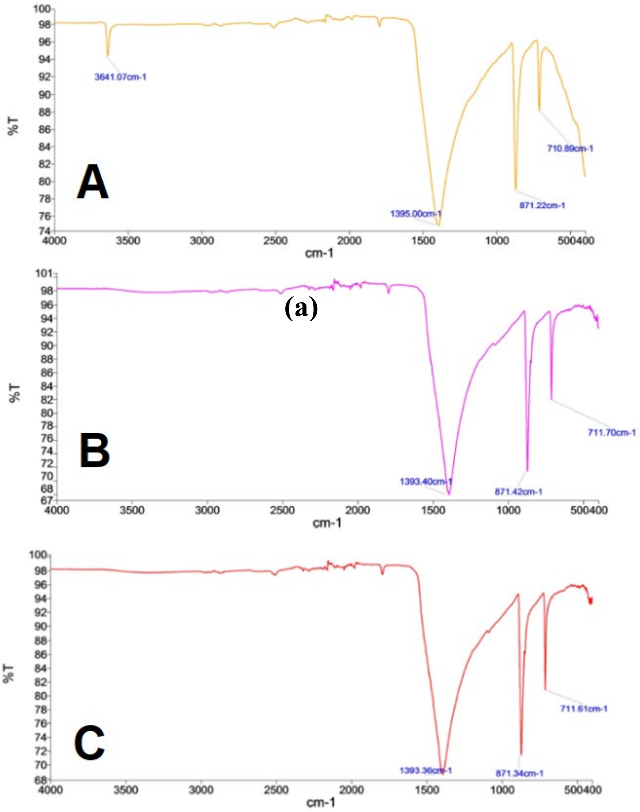

**Figure 3.** FTIR spectra of the CaO band of CCS (A), CaO band after the treatment time experiement (B), and CaO band after the dosage experiment (C).

Table 1 shows the functional groups that correspond to the FTIR band position. $CaCO_3$ in cockle shell exists in aragonite form, which is well known for its high biocompatibility and large surface area. Table 1 depicts the FTIR bond stretch for identifying the phase of the functional group calcium oxide, CaO, due to differences in their carbonate ions, $CO_3^{2-}$. Based on Table 1, there is a broad transmission band approximately at 3641.07 $cm^{-1}$ in the calcined cockle shell before adsorption, which is contributed to –OH stretching vibration from the synthetic wastewater. The prominent absorption peak of carbon band C–O was observed at 1393.36 $cm^{-1}$ before adsorption, 1393.36 $cm^{-1}$ with the analysis of dosages after adsorption, and 1393.40 $cm^{-1}$ with analysis of treatment time after adsorption, and the intensity is strong. The characteristic peaks defining carbonate ion, $CO_3^{2-}$ of aragonite cockle shell were between 700 and 900 $cm^{-1}$, which were at 710.89 and 871.22 $cm^{-1}$ before adsorption, 711.61 and 871.34

cm$^{-1}$ after adsorption with dosage analysis, and 711.70 and 871.42 cm$^{-1}$ after adsorption with treatment time analysis. These bands are related to the symmetric stretching modes of vibration and out-of-plane bending of vibration modes of $CO_3^{2-}$, respectively. The classification of the –OH band appearing at 3641.07 cm$^{-1}$ is the alcohol group with strong and broad intensity. This peak appears much broader than the other IR absorptions in the spectrum.

**Table 1.** FTIR spectrum explanation.

| Phase | Before/after adsorption | Type of analysis | FTIR band position (cm$^{-1}$) | Functional group |
|---|---|---|---|---|
| Calcium oxide (CaO) | Before adsorption | Without analysis | 710.89 | Carbonate ion |
| | | | 871.22 | Carbonate ion |
| | | | 1395.00 | C–O |
| | | | 3641.07 | OH |
| | After adsorption | Dosage | 711.61 | Carbonate ion |
| | | | 871.34 | Carbonate ion |
| | | | 1393.36 | C–O |
| | | Treatment time | 711.70 | Carbonate ion |
| | | | 871.42 | Carbonate ion |
| | | | 1393.40 | C–O |

### 3.3. Scanning Electron Microscopy (SEM)

SEM was used to observe the surface morphology of raw cockle shells (RCS) and calcined cockle shells (CCS). It shows the surface texture and porosity of the adsorbent to determine the surface availability for phosphorus adsorption on the adsorbent. Figure 4 (a) shows the SEM images of RCS, while Figure 4 (b) shows the SEM images of CCS. The average diameter of the cockle shell powder particles was 10 µm, indicating the availability of a net-work of porous surface textures that results in higher surface areas for phosphorus adsorption. The RCS micrograph shows a combination of stone and fine powder particles. On the other hand, the CCS micrograph illustrates a coral shape with spaces that grew larger as a result of the high calcination temperature. These spaces or porosity may be capable of trapping adsorbates during the physical adsorption process.

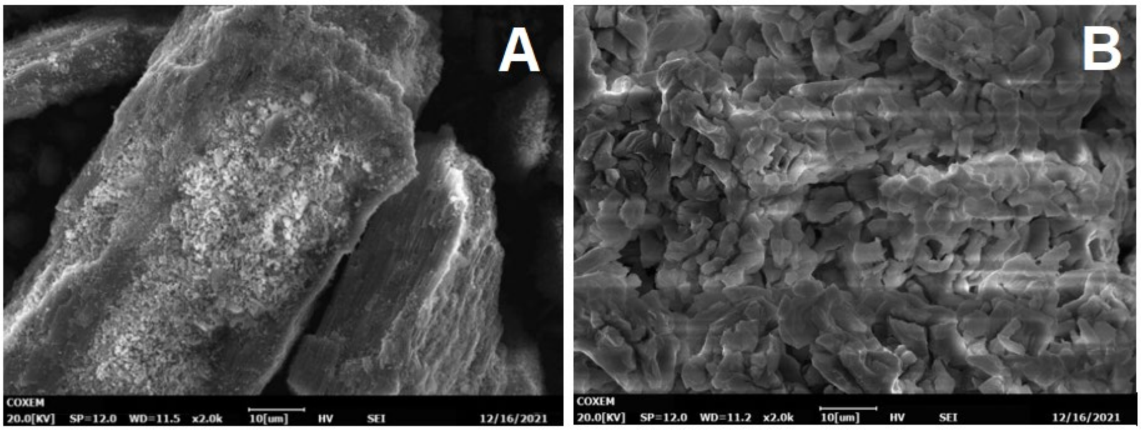

**Figure 4.** SEM photomicrograph of RCS before calcination under 2000× magnification (A) and CCS after calcination under 2000× magnification (B).

Table 2 shows the elemental composition of powdered cockle shell. Calcium has the highest percentage of elements inside the powdered cockle shell at 42.99%, while oxygen has 44.06%.

Ca and O combine to form CaO, so they effectively adsorb phosphorus. CaO was formed through the calcination process, which converted $CaCO_3$ to CaO [11].

**Table 2.** Elemental composition of powdered cockle shell.

| Element | wt % |
|---|---|
| O | 44.06 |
| Ca | 42.99 |
| C | 11.81 |
| Si | 0.51 |
| Na | 0.37 |
| Al | 0.26 |
| **Total** | **100.00** |

### *3.4. Effect of different adsorbent dosage*

Different adsorbent dosages were used to study the removal efficiency of phosphorus (E) and the adsorption capacity for phosphorus (q) from the synthetic wastewater solution. The adsorbent dosages used throughout the experiment were 0.2, 0.4, 0.6, 0.8, and 1.0 g. As shown in Figure 5, the phosphorus removal efficiency by CCS was proportional to the adsorbent dosage. As the adsorbent dosage increased from 0.2 to 1.0 g, the phosphorus removal efficiency by CCS increased from 87.65 % to 95.96 %. The higher removal percentage indicates that more phosphorus is attached to the adsorbent surface at that dosage. In essence, a higher adsorbent dosage results in more adsorption sites being available [12]. However, when adsorbent dosage was increased from 0.2 to 1.0 g, the phosphorus adsorption capacity of CCS decreased from 5.04 to 1.09 mg/g, as shown in Figure 5. According to the findings, the adsorbent has a consistent number of active adsorption sites at lower concentrations, implying that the adsorption site may adsorb more metal ions as shown in surface morphology (Figure 4). As the concentration increases, active sites may become saturated, causing the adsorption capacity to decrease. Surface saturation is one of the sorption properties that can influence the initial metal ion concentration in the solution.

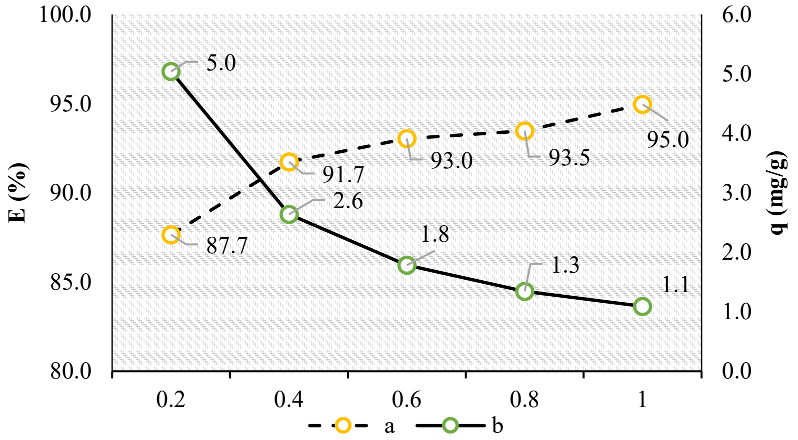

**Figure 5.** The effect of different CCS dosages on phosphorus removal: (a) phosphorus removal efficiency, E, and (b) adsorption capacity for phosphorus, q.

### *3.5. Effect of Treatment Time*

The effect of five different treatment times (20, 30, 40, 50, and 60 min) on the phosphorus removal efficiency and adsorption capacity of CCS was investigated. Phosphorus adsorption was initially quite fast, and longer contact times resulted in higher phosphorus removal, as shown in Figure 6. Phosphorus adsorption increased from 88.43 % to 95.74 % between 20 and 60 min. The increase in phosphorus adsorption may be due to the longer the contact period, which led to the availability of more adsorption sites on the adsorbent surface to adsorb the phosphate anions in the solution [13]. In brief, CCS is an ideal substrate for increasing the rate of phosphorus removal. When the duration of adsorption increased from 20 to 60 min, the phosphorus adsorption capacity of CCS increased from 1.02 to 1.10 mg/g.

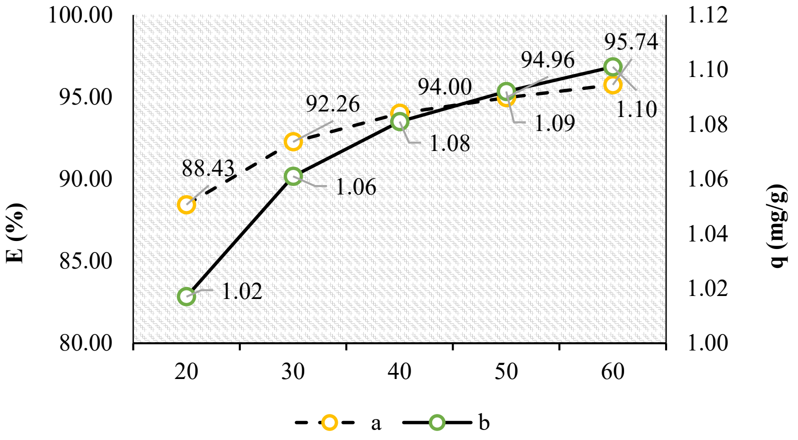

**Figure 6.** Effect of treatment time on phosphorus removal for CCS: (a) phosphorus removal efficiency, and (b) adsorption capacity for phosphorus.

## 4. Conclusions

CCS acted as a natural adsorbent and effectviely removed phosphate compounds from the synthetic wastewater solution. In this work, the calcined cockle shell powder with the highest dosage of 1.0 g removed 94.96 % phosphorus from the synthetic wastewater. Meanwhile, the treatment time of 60 min resulted in 95.74 % phosphorus adsorption. It is shown the potential of adsorbents to remove phosphate from water. Adsorption process using cockle shell waste is advantageous due to its low cost; therefore, further research of cockle shell adsorption may be useful and can potentially benefit the environment.

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## Competing Interest

The authors declare no conflict of interest.

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